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Alabaster, J. S.; Lloyd, R.
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FINELY DIVIDED SOLIDS

Foreword

A review of the literature on, and an attempt to define, tentative water quality criteria for finely divided solids and inland fish and fisheries were chosen as the first task of the Working Party on Water Quality Criteria for European Freshwater Fish and set a pattern for future reports. The preparation of the original report on which this chapter is based was accomplished largely by Mr D. W. M. Herbert, who prepared the basic manuscript for review by other members of the Working Party. It was not possible to study the whole of the world's literature on the subject, but a large proportion of the more important research reports was considered, together with unpublished data provided by fishery biologists in many European countries. Since then much more has been published including several reviews, e.g. by Hollis *et al.* (1964), Shelton and Pollock (1966), Gammon (1970), Ritchie (1972), and Sorensen *et al.* (1977); the data support the conclusions drawn in the original EIFAC report and therefore are not reviewed again here, except in a few cases where European species are concerned. In addition, hitherto unpublished data are included.

1.1 Summary

Water quality criteria for suspended solids are needed by those who have to manage inland fisheries and must sometimes decide, for example, how much solid matter could enter a river or lake without undue risk to a fishery, or whether it is worth attempting to develop a commercial or recreational fishery in water already containing a known concentration of such materials.

There are at least five ways in which an excessive concentration of finely divided solid matter might be harmful to a fishery in a river or a lake. These are:

(a) By acting directly on the fish swimming in water in which solids are suspended, and either killing them or reducing their growth rate, resistance to disease, etc.

(b) By preventing the successful development of fish eggs and larvae.
(c) By modifying natural movements and migrations of fish.
(d) By reducing the abundance of food available to the fish.
(e) By affecting the efficiency of methods for catching fish.

Some or all of these factors could operate together to harm a fishery.

There is evidence that not all species of fish are equally susceptible to suspended solids, and that not all kinds of solids are equally harmful. Unfortunately there is very little information on these and many other aspects of the problem, and much of the evidence which does exist is less firmly established than is desirable. It has therefore been concluded that definite water quality criteria which distinguish between the many different kinds of finely divided solids to which different sorts of inland fisheries may be subjected cannot yet be proposed. Nevertheless, when the evidence is considered as a whole, certain general conclusions can be drawn.

There is probably no sharply defined concentration of a solid above which fisheries are damaged and below which they are quite unharmed. It appears that any increase in the normally prevailing concentration of suspended matter above quite a low level may cause some decline in the status and value of a freshwater fishery, and that the risk of damage increases with the concentration. Although there is not enough evidence to allow the relation between solids concentration and risk of damage to be defined at all precisely, the Working Party considers that the degree of risk to fisheries may be divided into four arbitrarily defined categories and that rough estimates may be made of the ranges of concentration to which they would generally correspond. From this approach to the problem the following tentative criteria are presented. With respect to chemically inert solids and to waters which are otherwise satisfactory for the maintenance of freshwater fisheries,

(a) There is no evidence that concentrations of suspended solids less than 25 mg/ℓ have any harmful effects on fisheries.
(b) It should usually be possible to maintain good or moderate fisheries in waters which normally contain 25–80 mg/ℓ suspended solids. Other factors being equal, however, the yield of fish from such waters might be somewhat lower than from those in category (a).
(c) Waters normally containing from 80–400 mg/ℓ suspended solids are unlikely to support good freshwater fisheries, although fisheries may sometimes be found at the lower concentrations within this range.
(d) At the best, only poor fisheries are likely to be found in waters which normally contain more than 400 mg/ℓ suspended solids.

In addition, although concentrations of several thousand mg/ℓ solids may not kill fish during several hours or days exposure, such temporary high concentrations should be prevented in rivers where good fisheries are to be maintained.

The spawning grounds of salmon and trout require special consideration and should be kept as free as possible from finely divided solids.

1.2 Introduction

Nearly all river and lake waters have some solid matter in suspension and some times, contain very high concentrations resulting from soil erosion, fr

engineering works during which large volumes of earth are disturbed, from forestry operations, and from the discharge of sewage, sewage effluents, mining wastes, pulp and paper mill wastes, and other industrial effluents. Solids of many different kinds are therefore to be found in surface waters. Some of them—basic salts of zinc for example—have toxic properties (Lloyd, 1960; Herbert and Wakeford, 1964), while organic solids are oxidized by micro-organisms which can reduce the concentration of dissolved oxygen to levels at which fish are asphyxiated. Effects of these kinds are not considered in this chapter, nor has particular attention been given to the effects which solids may have by altering physical characteristics of the water such as temperature. Furthermore, some waste waters contain both solids in suspension and potentially harmful substances in solution.

The possibility that suspended solids will modify the resistance of fish to poisons, or to low dissolved oxygen, high temperature and extremes of pH value has not been examined, nor are there included in the chapter the results of laboratory studies or of observation in the field unless it was reasonably certain that any adverse effects were due only to the solids. For example, Rolley and Owens (1967) have shown that dissolved oxygen may be reduced as a result of deposits of organic matter being brought into suspension, consequently we have not used some reports of fish kills during floods when the suspended-solids concentration was high and the dissolved-oxygen concentration was not measured.

Some other research reports have been excluded because we considered that the conclusions reached by their authors were not fully supported by the evidence. In many research papers—especially some of those reporting studies of lakes and rivers—much of the evidence which we have used is less securely established than is desirable because the suspended-solids concentrations were not measured very often.

Although most authors have reported their observations as weight of solids per unit volume of water, others have expressed them as light transmittancies of Secchi disc readings. One of these systems of measurement cannot be converted into another unless the relation between them has been determined for the particular solid under consideration. Because the appropriate relation has seldom been reported, we have not attempted to use one system of measurement throughout the literature survey, but have quoted results in the units employed by the authors.

From our study of the literature it is apparent that there are at least five ways in which an excessive concentration of finely divided solid matter might be harmful to a fishery in a river or a lake. These are:

(a) By acting directly on the fish swimming in water in which solids are suspended, and either killing them or reducing their growth rate and resistance to disease.
(b) By preventing the successful development of fish eggs and larvae.
(c) By modifying natural movements and migrations of fish.
(d) By reducing the abundance of food available to the fish.
(e) By affecting the efficiency of methods for catching fish.

In addition, some or all of these factors could operate together to harm a fishery. These subjects (except (e)) are considered in the next se[...] this chapter.

1.3 Literature survey

1.3.1 DIRECT EFFECTS OF SOLIDS IN SUSPENSION

Death or survival of fish

Wallen (1951) kept several species of fish in water containing montmorillonite clay and increased the turbidity to high levels for a short time each day by stirring the sediment. Most individuals of all species–including goldfish (*Carassius auratus*) and common carp (*Cyprinus carpio*)–endured maximum turbidities of 100 000 mg/ℓ occurring during experiments lasting a week or more, and some individuals of these two species survived occasional exposure to 225 000 mg/ℓ for one to three weeks. Herbert (personal communication) found that rainbow trout (*Salmo gairdneri*) survived one day in 80 000 mg/ℓ silt from gravel washing, and the concentration had to be raised to about 160 000 mg/ℓ to kill them within this period. J. S. Alabaster (personal communication) found that harlequin (*Rasbora heteromorpha*), a tropical fish, was killed in a day by about 40 000 mg/ℓ bentonite clay, but survived for a week in 6000 mg/ℓ. Resuspended harbour sediment (containing organic matter, oil and grease, and heavy metals at concentrations of up to 28 000 mg/ℓ) had no observable adverse effects on stickleback (*Gasterosteus aculeatus*) and fry of coho salmon (*Oncorhynchus kisutch*) in 4 days (Le Gore and Des Voigne, 1973). Cole (1935) reported that some fish survived 20 000 mg/ℓ wood fibre, although he said that it undoubtedly hastened the death of unhealthy or moribund individuals, and Griffin (1938) stated that Pacific salmon (*Oncorhynchus*) and trout fingerlings lived for 3–4 weeks in concentrations of 300–750 mg/ℓ silt which were increased to 2300–6500 mg/ℓ for short periods by stirring the sediment each day. Thus it appears that many kinds of fish are unlikely to be killed within a day or so by exposure to suspended matter unless the concentrations are extremely high. To kill within such short times the concentrations of some solids would probably have to exceed 100 000 mg/ℓ. However, Slanina (1962) found that although rainbow trout survived a week in 5000–300 000 mg/ℓ suspended mineral solids, the epithelium of their gills had thickened and proliferated. Similarly-affected gills were observed in rainbow trout which eventually died after exposure to several hundred mg/ℓ solids for longer periods (Herbert and Merkens, 1961). Exposure for relatively short periods to very high concentrations might thus be harmful eventually even though fish are not killed within the period of exposure.

Concentrations of several hundred thousand mg/ℓ are never likely to be present in surface waters for more than a short time, but quite high concentrations can be present for relatively long periods. From 2000 to 6000 mg/ℓ silt, persisting for 15–20 days, have been reported for rivers in flood (Campbell, 1954; Simaika, 1940; and Kemp, 1949); 6000 mg/ℓ and 1000 mg/ℓ appear to have been average levels in two streams continuously polluted with wastes from china-clay mining (Herbert *et al.*, 1961).

In the laboratory, 4250 mg/ℓ gypsum in suspension produced a 50 per cent mortality among rainbow trout in about 3½ weeks (Herbert and Wakeford, 1962). Caged rainbow trout were killed in 20 days in the Powder River, Oregon, when the concentration was 1000 to 2500 mg/ℓ but other conditions were apparently satisfactory (Campbell, 1954). In laboratory studies there were 40–50 per cent kills of trout in 810 and 270 mg/ℓ kaolin and diatomaceous

earth after exposure periods of 10 days in some experiments, but only after 85 days in others (Herbert and Merkens, 1961). Spruce fibre at 200 mg/ℓ produced 50 per cent mortality among rainbow trout after 16 weeks exposure, and 70 per cent after 30 weeks (Herbert and Richards, 1963).

On the other hand, M. Grande (personal communication) found that only one rainbow trout out of five was killed during 37 days in 1000 mg/ℓ cellulose fibre, and Vallin (1935) reported that one individual of each of the species *Carassius carassius*, *Leuciscus rutilis*, and *Thymallus thymallus* was tested and survived 3 weeks in 200 mg/ℓ. Herbert and Wakeford (1962) found that there were no deaths among rainbow trout kept for 4 weeks in a suspension of 553 mg/ℓ gypsum. There was 100 per cent survival of the same species for 9 to 10 months in 200 mg/ℓ of solids from a coal washery (Herbert and Richards, 1963).

Thus there is evidence from properly conducted experiments and reliable observations of rivers that suspended-solids concentrations from 200 to several thousand mg/ℓ have caused deaths among fish exposed for several weeks or months, and other equally reliable evidence that fish have been kept with few or no deaths at concentrations in the range 200–1000 mg/ℓ for similar periods. These differences are probably due in part to the kind of solid: in simultaneous experiments with identical techniques, all the rainbow trout tested in 200 mg/ℓ coal washery solids for 40 weeks survived, whereas nearly 80 per cent died in the same concentration of spruce fibre (Herbert and Richards, 1963). Ellis (1944) states that the larger the particles, and the greater their hardness and angularity, the greater the possibility of injury to gill structures. Another factor is that species of fish are not all equally resistant. Smith, Kramer and McLeod (1965) found that walleye fingerlings (*Stizostedion v. vitreum*) were killed within 72 hours by 100 mg/ℓ of various wood pulps, although 20 000 mg/ℓ did not kill fathead minnow (*Pimephales promelas*) exposed for 96 hours. Whether or not fish in a river or lake will eventually be killed by the continual presence of 200 mg/ℓ suspended solids or more is likely to depend upon the nature of the solids and the species present. Nevertheless, the available evidence suggests that the death rate among fish living in waters which over long periods contain suspended solids in excess of 200 mg/ℓ will often be substantially greater than it would have been in clean water.

There are also a few studies of death rates in concentrations lower than 200 mg/ℓ. Smith, Kramer and McLeod (1965) found that the walleye (which seems to be an extremely sensitive fish) was killed within 3 days by 100 mg/ℓ wood pulp, and a rather special case is provided by ferric hydroxide which when precipitated from acid solutions containing 3 mg/ℓ Fe on to the gills of trout, carp, and tench (*Tinca tinca*) kills them when the pH value rises above 5.5 (H. Mann, personal communication; Krämer, 1924). More recent work by Sykora, Smith and Synak (1972) showed that suspensions of ferric hydroxide of about 96, 48 and 24 mg/ℓ caused juvenile brook trout (*Salvelinus fontinalis*) to reach no more than 16 per cent, 45 per cent and 75 per cent of the weight of control fish and they attributed the effect to reduced feeding caused by impaired visibility of the food.

In the majority of reported cases, however, death rates in 100 mg/ℓ and less have been little or no higher than among control fish in clean water. Herbert and Merkens (1961) found that rainbow trout kept for long periods in 90 mg/ℓ kaolin and diatomaceous earth suffered a slightly higher death rate than did the control fish, but the mortality was low: in five out of six tests lasting for 2–6 months

months exposure to 100 and 50 mg/ℓ spruce fibre or coal washery waste solids (Herbert and Richards, 1963), and no significant increase over control mortality among the same species in 30 mg/ℓ kaolin or diatomaceous earth (Herbert and Merkens, 1961).

Growth

The growth (and survival) of larval lake herring (*Coregonus artedii*) were not affected during exposure for 62 days to a concentration of red-clay of up to 28 mg/ℓ (Swenson and Matson, 1976). Laboratory experiments, in which trout were given equal quantities of food in amounts which were nearly enough to satisfy their appetites, showed that 50 mg/ℓ wood fibre or coal washery waste solids reduced their growth rate, and that they grew more slowly as the suspended-solids concentration was increased (Herbert and Richards, 1963). Nevertheless the fish grew reasonably well in the presence of the abundant food supply; even in 200 mg/ℓ coal washery waste solids, yearling fish more than trebled their weight in 8 months.

Resistance to disease

Herbert and Merkens (1961) found that rainbow trout in 270 mg/ℓ diatomaceous earth suffered more from the disease 'fin-rot' than controls in clean water. Herbert and Richards (1963) report that many of the rainbow trout dying in 200 mg/ℓ wood fibre suffered from fin-rot, and that fish in 100 mg/ℓ showed some symptoms after 8 months, although those in 50 mg/ℓ and the control fish showed no sign of the disease.

1.3.2 SUSPENDED SOLIDS AND REPRODUCTION

If solids settle from suspension and block gravel which contains eggs, high mortalities will result. Shapovalov (1937) showed that silting reduced the survival of rainbow trout eggs (*Salmo gairdnerii*) in gravel, and found the same with silver salmon (*Oncorhynchus kisutch*) eggs in later experiments (Shapovalov and Berrian, 1940). Hobbs (1937) states that the mortality of trout eggs in New Zealand streams was greatest in those redds which contained the greatest proportion of material smaller than 0.03 inch in diameter. According to Ward (1938) who studied the Rogue River, Oregon, where placer mining was extensively practised, '. . . erosion silt in some streams has been found to cover nests and spawning grounds with a blanket such that the bottom fauna was killed and eggs also suffocated in nests.' Campbell (1954) planted eggs in gravel in the Powder River, Oregon, where the turbidity was between 1000 and 2500 ppm as a result of mining operations. All the eggs died in 6 days, although there was only 6 per cent mortality in 20 days at a control site where the water was clean. Other instances of eggs being killed by siltation are given by Heg (1952), Hertzog (1953), Gangmark and Broad (1955 and 1956), and Neave (1947).

Stuart (1953) has shown that Atlantic salmon (*Salmo salar*) and brown trout (*Salmo trutta*) eggs—which are buried in gravel on the stream beds—can develop successfully only if a current of water passes through the gravel, while Gangmark and Bakkala (1960) found that the survival of king salmon (*Oncorhynchus tshawytscha*) eggs increased with the velocity of water through the gravel in which they were laid. Fish eggs require oxygen during development. Alderdice, Wickett and Brett (1958) showed that chum salmon (*Oncorhynchus keta*) eggs needed at least one part oxygen per million in the surrounding water at the early stages and 7 ppm at later stages if they were to hatch successfully, and Alderdice and Wickett (1958) demonstrated that the utilization of oxygen by the eggs was impaired by increasing the carbon dioxide concentration. Wickett (1954) concluded that the amount of oxygen available to eggs depends not only on its concentration in the water, but also upon the rate at which the water flows over the eggs.

The foregoing observations are relevant to the silting up of spawning beds after the eggs have been laid, but there is also evidence that some salmonids will not spawn in gravel which is already blocked. Stuart (1953) found that brown trout do not dig redds in gravel if it is choked with sediment, nor will they do so even if the surface has been cleared of sediment so that it appears indistinguishable from known spawning areas; presumably this is because the fish detects that water is not flowing through the gravel. Rather similar behaviour was observed with cutthroat trout (*Salmo clarkii*); these fish abandon a redd if they encounter silt while they are digging (Snyder, 1959).

Where the harm is done by blocking gravel spawning beds, the concentration of solids suspended in the water is apparently less important than the amount which will settle out of suspension. This will depend upon such factors as the size of the solid particles, the stream velocity and degree of turbulence. Some rivers in British Columbia support large populations of Pacific salmon (*Oncorhynchus*) in spite of carrying heavy loads of glacial silt. Spawning takes place, however, when the rainfall is heavy and silt is flushed out of the spawning beds (Foskett, 1958).

Finely divided solids can be harmful to eggs which are not buried in spawning beds. Stuart (1953) observed that silt in suspension will adhere to the surface of eggs and kill them—probably by preventing sufficient exchange of oxygen and carbon dioxide between the respiring egg and the water. Suspended solids can damage the eggs of species which do not lay them on or in stream beds. The eggs of the yellow perch (*Perca flavescens*), which are laid in gelatinous strings entwined round aquatic plants, etc., were mostly destroyed over an area where silt from the construction of a road increased the turbidity to give an average Secchi disc reading of 0.46 m, but hatching was reasonably successful above the silted area where the average Secchi disc reading was 0.84 m (Muncy, 1962). Pikeperch (*Stizostedion lucioperca*) eggs are also entwined around plants and have been killed in Lake Balaton when the suspended solids content of the water rises during storms (Wynárovich, 1959). On the other hand the survival of eggs of walleye was not affected by wood fibre at a concentration of 250 mg/ℓ, even when the concentration of dissolved oxygen was 33 per cent of the air saturation value (Kramer and Smith, 1966).

1.3.3 SUBLETHAL EFFECTS AND EFFECTS ON BEHAVIOUR

Quite high concentrations of suspended solids in part of [illegible] do not stop salmonid fish from passing through on migration between [illegible] and sea water.

There are Atlantic salmon in the River Severn in the British Isles and they are netted in the estuary although parts of the estuary naturally contain high concentrations of suspended solids—up to several thousand mg/ℓ at times (Gibson, 1933). Smith and Saunders (1958), when studying the movements of brook trout between fresh and salt water, found that turbidity seemed to have no effect on the fish's movements. Ward (1938) said that the normal concentrations of suspended solids in several Oregon streams were 137-395 mg/ℓ and that salmon run through them. On the other hand, when given a choice, some fish will select clear water. Thus, Sumner and Smith (1939) found that king salmon avoided the muddy water of the Yuba River, California, and entered a clean tributary. These fish also chose a clear streak in a muddy river for spawning rather than more turbid areas nearby. Schools of minnow advancing down a clean tributary to a muddy river have been seen to turn back immediately their heads enter the water of the muddy stream (Moore, 1932).

Bachmann (1958) found that when cutthroat trout in a river in Idaho were subjected for two hours to a turbidity of 35 mg/ℓ they were unharmed, but sought cover and stopped feeding.

Hofbauer (1963), when studying the factors influencing the numbers of migrating fish passing through a fish ladder, considered that the tendency for the barbel (*Barbus barbus*) to migrate decreased with increasing turbidity of the water, even though other conditions such as temperature and water level would favour migration. The opposite tendency appeared to be the case with the European eel (*Anguilla anguilla*): migration occurred when there was notable turbidity, and migration intensity decreased immediately the water became clearer. Ventilation rates of green sunfish (*Lepomis cyanellus*) were affected by concentrations of bentonite clay suspensions greater than about 17 800 mg/ℓ at 5 °C, 13 300 mg/ℓ at 15 °C and 6700 mg/ℓ at 25 °C, but rates of oxygen consumption were not affected by concentrations as high as about 26 700 mg/ℓ (Horkel and Pearson, 1976). However, Heimstra and Damkot (1969) found that turbid conditions reduced the activity and affected normal hierarchical behaviour of this species.

1.3.4 EFFECT ON FOOD SUPPLY

The amount of food for fish in fresh waters depends ultimately upon the growth of green plants (algae and higher aquatic plants). Such plants may be restricted by suspended solids; for example, severe abrasive leaf damage by coal dust to the aquatic moss (*Eurhynchium ripariodus*) was observed at 500 mg/ℓ after one week and at 100 mg/ℓ after three weeks (Lewis, 1973). On the other hand, Hynes (1970) reported that a fairly even discharge, containing silt, can create great stable areas of weed development which can completely alter the substratum (directly and indirectly) and with it the animal population. The considerable literature on this indirect effect on fisheries is not considered in detail in this chapter.

We have found few laboratory studies on the concentrations of suspended solids which can be tolerated by invertebrate animals on which fish feed. Stephan (1953) worked with several Cladocera and Copepoda. The harmful effect of suspended solids on these animals was thought to be partly due to clogging of their filter-feeding apparatus and digestive organs, and the critical concentrations were 300-500 mg/ℓ. Clay was most harmful, while earth and sand caused less

damage. Robertson (1957) studied the survival and reproduction rate of *Daphnia magna* in suspensions of several kinds of solids. Apparently harmful levels were:

Kaolinite	392 mg/ℓ
Montmorillonite	102 mg/ℓ
Charcoal	82 mg/ℓ

82 - 500 mg/L

Pond sediment was not lethal up to 1458 mg/ℓ. After being washed with hydrochloric acid, montomorillonite, pond sediment and charcoal were more toxic. Different kinds of solids thus appear to have different toxicities, and Robertson considers that this may be attributed, at least in part, to differences in absorptive capacity. Much lower concentrations (e.g. 39 mg/ℓ kaolinite, 73 mg/ℓ pond sediment) appeared to increase the reproduction rate of *Daphnia*.

Although they are often important in lakes, small planktonic invertebrates like *Daphnia* are a less important component of the fish-food fauna in rivers than organisms which live on the stream bed or on plants. Benthic animals are at risk not only from the solids in suspension, but from the accumulation of particles which settle on the bottom. Many authors have reported more or less severe reductions in bottom fauna from this cause. Thus, Taft and Shapovalov (1935) studied the abundance of the fauna on the beds of Californian streams into which large quantities of natural silt were washed by mining operations. In samples taken during the summer there were always fewer food organisms per unit area in the places where mining was practised than in clear streams. In the Scott River, silted areas averaged about 300 organisms m^{-2} (36 ft^{-2}), while in clean areas the average was about 2000 m^{-2} (249 ft^{-2}). Smith (1940) quotes earlier work by Surber and Smith which showed that silted areas in the American and Yuba Rivers of California contained only 41-63 per cent as many food organisms on the stream beds as did clear streams. Tebo (1955) found that in North Carolina streams heavy siltation caused by dragging logs over the ground near a small tributary resulted in turbidities of 261-390 mg/ℓ in a trout stream, and during summer and autumn, when the flow of water was low, the stream bed was covered with a layer of sterile sand and micaceous material up to 254 mm (10 inches) deep. In these areas the bottom fauna was only one-quarter as abundant (as volume per unit area) as at clean places above the point where the silt entered. Rainbow trout fed mainly on bottom fauna from January to June, but from June to December this made up only 42 per cent of their food, much of the remainder consisting of terrestrial insects. The bottom fauna (expressed as wet weight per unit area) in clean Cornish streams was found by Herbert *et al.* (1961) to be present at nine times the density occurring in streams containing 1000 and 6000 mg/ℓ suspended solids, although in a stream with an average of 60 mg/ℓ the bottom fauna was about equal in abundance to that in the clean rivers. These authors found during their survey that although a substantial proportion of the food eaten by trout (in May) consisted of bottom fauna, much of the food consisted of terrestial forms. Even a complete destruction of aquatic invertebrates in these streams did not mean that no food was available for those fish, but only that the total quantity was reduced. The effects on the food supplies of other species might be more serious. Gammon (1970) studied a stream where the concentration of suspended solids increased from a range of 13-52 mg/ℓ upstream of a limestone quarry to a range of 21-250 mg/ℓ downstream. Although the numbers of some invertebrate species (of the Trichcorytholdes) that preferred a silt or mud substrate increased below the quarry; those of others (the net-spinning species of *Cheumatopsyche*) were reduced during periods of high concentrations. Also the drift rate of macroinvertebrates from an impacted riffle increased with concentration of suspended solids, the increase being 25 per cent with a concentration increase of 40 mg/ℓ above normal and 90 per cent at 80 mg/ℓ above normal.

Several more examples are given in unpublished reports of investigations made in France for administrative purposes and summarized for us by M. P. Vivier. Waste water from a sand-washing plant contained 29 900 mg/ℓ suspended solids, of which 19 750 mg/ℓ was settleable. When discharged to a trout stream in the Côtes du Nord it caused the disappearance of the bottom fauna of Trichoptera (*Hydropsyche, Rhyacophiles*), Ephemeroptera (*Ecdyonurus*), Crustacea (*Gammarus*) and Mollusca (*Ancylus, Limnea*) which were present upstream. Four kilometres downstream, where the suspended-solids concentration had fallen to 29 mg/ℓ, the fauna reappeared except for the Ephemeroptera. Plants and fish-food fauna disappeared from another trout stream after introduction of 250 mg/ℓ suspended solids from a quarry. Another small stream in the Vosges contained 11 300 mg/ℓ solids just below a granite crushing mill and washing plant, and 185 mg/ℓ 7 km downstream at its confluence with the R. Saône. The normal fauna and flora were completely absent from the tributary below the discharge. Coal mines brought the suspended solids in a river in the Gard Department to 570 mg/ℓ 1 km below the pits, and the river was virtually abiotic for 10 km. After this distance the suspended-solid concentration had fallen to about 100 mg/ℓ and a sparse fauna reappeared.

Although the bottom fauna of streams may be drastically reduced by finely divided solids which are chemically inert, deposits of some kinds of organic solids—humus from a sewage-disposal works for example—can support dense populations of some bottom-dwelling invertebrates, such as *Chironomus riparius* and *Asellus aquaticus*, which provide an abundant food supply for fish (Allan, Herbert and Alabaster, 1958).

1.3.5 THE TOTAL EFFECT OF SUSPENDED SOLIDS ON FRESHWATER FISHERIES

The earlier sections of this review have shown that sufficiently high concentrations of suspended solids can kill fish directly, increase their susceptibility to disease, reduce their rate of growth, modify their normal movements within fresh water, reduce the area suitable for spawning, and kill developing eggs. In addition, the quantity of natural food available to fish can be reduced. When a freshwater fishery is harmed by excessive quantities of finely divided solid matter, it is likely that many of these factors will be operating, although the relative importance of each one will probably not be the same in every case. Correlation of the status of fisheries in lakes and rivers with the concentrations of solids found in them should therefore provide data very relevant for the establishment of water quality criteria.

Ellis (1937) made 514 determinations of turbidity at 202 places on rivers in the U.S.A., and classified each site as either having or not having a good mixed fish fauna. His results are summarized in *Figure 1.1*. Precise conclusions cannot be drawn from these data, because few measurements of turbidity were made at most sites and these might not adequately represent the levels occurring in

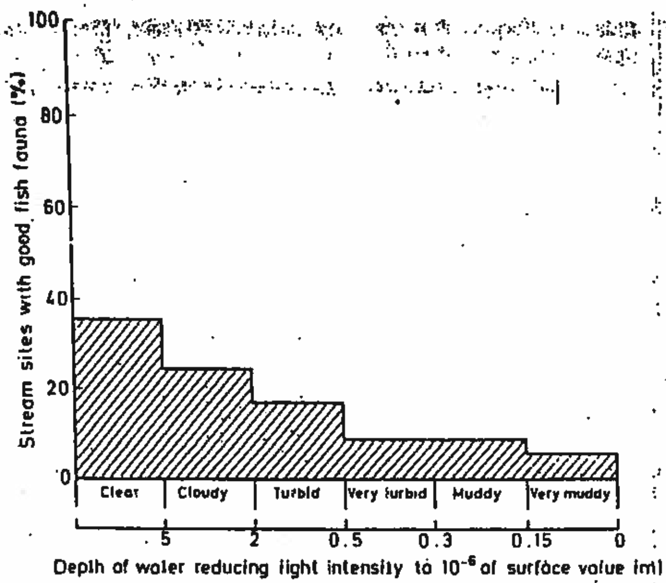

Figure 1.1 Turbidity and freshwater fisheries in the U.S.A. Data from Ellis (1937) (514 determinations of turbidity were made at 202 river stations)

rivers where turbidity can fluctuate considerably. Furthermore, a poor fish population may not have been due to high turbidity in every case but to some other factor such as low dissolved oxygen (see p. 3, para. 2). Nevertheless, the data of Ellis suggest that an increase in turbidity above quite low levels will reduce the chances of maintaining a good fishery, although it should be noticed that good fish populations were found at a few places where the water was very muddy.

It seems that some species of fish are much more tolerant of muddy water than others, and that an increase in suspended solids can lead to an increase in the numbers of the resistant fish as they are freed from competition with less tolerant species. Aitken (1936) said that Iowa streams which once supported trout, smallmouth black bass (*Micropterus dolomieui*), and other clean-water species were transformed by excessive soil erosion so that they contained rough fish or mud-loving forms. Similar changes in parts of the Ohio river basin are reported by Trautman (1933). Rather more detailed evidence of changes which could eventually alter the species composition of a fishery is provided by an investigation made by the Institute of Freshwater Research, Drottningholm,

Table 1.1

Secchi disc reading (mm)	*No. of nets*	*No. of whitefish caught per net*
100-200	11	0.6
400-500	15	1.0
> 1000	10	1.9

which indicated that erosion turbidity in Lake Hotögeln, Sweden, was probably responsible for greatly reduced catches of char (*Salvelinus alpinus*), although the catches of trout and European grayling (*Thymallus thymallus*) were not appreciably affected. *Table 1.1* shows that the catch of whitefish (*Coregonus lavaretus*) in Lake Aisjaur, Sweden, was reduced by turbidity due to mining wastes consisting principally of quartz sand. The catches of perch (*Perca fluviatilis*) and pike (*Esox lucius*) were, however, not affected (Vallin, personal communication). Doan (1942) investigated the fishery statistics for Lake Erie where the turbidities vary between 5 and 230 mg/ℓ. The annual commercial catch of 'yellow pickerel', i.e., the walleye (*Stizostedion v. vitreum*), was inversely correlated to a statistically significant extent with the turbidities during April and May of the same year. On the other hand the catch of sauger (*Stizostedion canadense*) was positively correlated with the turbidities prevailing three years earlier.

Whitefish (*Coregonus* sp.) have suffered severely from suspended solids in several lakes. Many species of whitefish feed mainly on plankton, and typically dwell in lakes where the water is clear and cold. Scheffel, quoted in Stephan (1953), recounts the history of the fishery in the Chiemsee, Upper Bavaria, where suspended solids carried in by streams appear to have been responsible for a decline in the whitefish catch to a few under-nourished fish in 1920, and to zero over the period September 1920 to February 1921. The number of spawning fish was also severely reduced. Previously these fish had fed on zooplankton which was presumably abundant enough for their needs, but the reduced population was feeding on bottom-dwelling animals such as snails and chironomid larvae. Similar observations were made by Einsele (1963) on the Mondsee in Austria. Some large quantities of clay entered this lake during the construction of a road in 1961–62, making the water very turbid. This reduced the development of plankton, particularly *Daphnia*. Einsele estimated that the normal annual production of *Daphnia* in the Mondsee was about 400 000 kg fresh weight, and this fell to 80 000 kg in the turbid conditions. The turbidity also increased the mortality rate of the whitefish, resulting in a very low catch the following year.

Schnedeberger and Jewel (1928) studied ponds in the U.S.A. which naturally contained different concentrations of suspended solids, and found that the production of fish increased as turbidity was reduced down to a value of 100 mg/ℓ. Buck (1956) studied the growth of fish in 39 farm ponds, having a wide range of turbidities, which were cleared of fish and then restocked with largemouth black bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*) and red-ear sunfish (*Lepomis microlophus*). After two growing seasons the yields of fish were:

Clear ponds	(< 25 mg/ℓ suspended solids)	161.5 kg/ha
Intermediate	(25–100 mg/ℓ suspended solids)	94.0 kg/ha
Muddy	(> 100 mg/ℓ suspended solids)	29.3 kg/ha

The rate of reproduction was also reduced by turbidity and the critical concentration for all three species appeared to be about 75–100 mg/ℓ. In the same paper, Buck reports that largemouth black bass, crappies (*Pomoxis*) and channel catfish (*Ictalurus punctatus*) grew more slowly in a reservoir where the water had an average turbidity of 130 mg/ℓ than in another reservoir where the water was always very clear.

In rivers, Herbert *et al.* (1961) found that 1000 and 6000 mg/ℓ china-clay wastes had reduced the populations of brown trout to about one-seventh the

density found in clean streams, but that a normal trout population was present in a river carrying 60 mg/ℓ. There is much additional evidence in the unpublished reports from France communicated to us by P. Vivier. In a river in the Gard Department of France which supports a cyprinid fish fauna, fish are absent from a stretch which contains up to 570 mg/ℓ solids from coal mines, but a few roach and chub reappear 10 km below the mines where the suspended-solids concentration has fallen to about 100 mg/ℓ. Trout, minnow and bullhead which populate the upper reaches of a stream in the Vosges, disappear completely below the entry of wash waters from a granite-crushing mill which raises the suspended-solids content to 11 300 mg/ℓ immediately below the discharge. The fish do not reappear until the confluence of the stream with the R. Saône: just above the confluence 185 mg/ℓ suspended solids are present. Trout and dace were present in a stream in the Finistère Department of France above the entry of wash water from a tin mine, but the only fish in the polluted zone were eels. When the suspended solids were determined in this stream during a flood, 560 mg/ℓ were present 500 m below the discharge, and 80 mg/ℓ 4 km below. A rich fauna of Ephemeroptera, Trichoptera, Crustacea, Mollusca and worms almost completely disappeared below the discharge. However, in mountain streams fed by melting snow, some 1000 mg/ℓ suspended solids are often present for three to five months of the year and trout are found there, although not in large numbers. In the R. Loireiva (Norway), which is rather muddy with an average concentration of about 50 mg/ℓ suspended solids but with occasional concentrations up to 1331 mg/ℓ, pike, perch, pikeperch and several species of cyprinids are common. A very similar fish fauna is found in another muddy Norwegian stream, the Nitelva, in which the concentration range is 5.9–99.8 with an average of about 25 mg/ℓ, and in the R. Leira where the median and 95 percentile values were 58 and 250 mg/ℓ (M. Grande, personal communication). In the R. Trent catchment (U.K.) the maximum annual 50 and 95 percentile concentrations of suspended solids during the period 1968 to 1972 in areas where fish occurred were 18 and 412 mg/ℓ respectively for trout, and 62 and 965 respectively for coarse fish (J. S. Alabaster and I. C. Hart, personal communication). D. W. M. Herbert (personal communication) installed a suspended-solids recorder for a year in the R. Mimram, Hertfordshire, where there was a good trout fishery, and found that the average suspended-solids concentration was 24 mg/ℓ with maximum values of 80–100 mg/ℓ occurring at times. Liepolt (1961) reports that a trout fishery existed in a stream usually containing 19–23 mg/ℓ solids, and that this was not harmed by dredging operations which raised the concentration to about 160 mg/ℓ for short periods, except that fly-fishing was impeded when the water was turbid. Peters (1957) studied a trout stream containing suspended solids of agricultural origin and found good populations at one station where the median and 95 percentile values were 18 and 35 mg/ℓ, slightly reduced numbers where the percentiles were 70 and 180 mg/ℓ respectively, and a 75 per cent reduction where they were 160 and 300 mg/ℓ respectively. More recently Gammon (1970) found that in a stream in which the concentration of suspended solids increased from a range of 13–52 mg/ℓ upstream of a limestone quarry, to a range of 21–250 mg/ℓ below it, most fish, including common carp, were reduced in numbers downstream.

Herbert and Richards (1963) report the results of a questionnaire sent to River Boards in England, Scotland and Wales. Streams containing suspended solids of industrial origin were classified as either 'Fish present' [illegible]

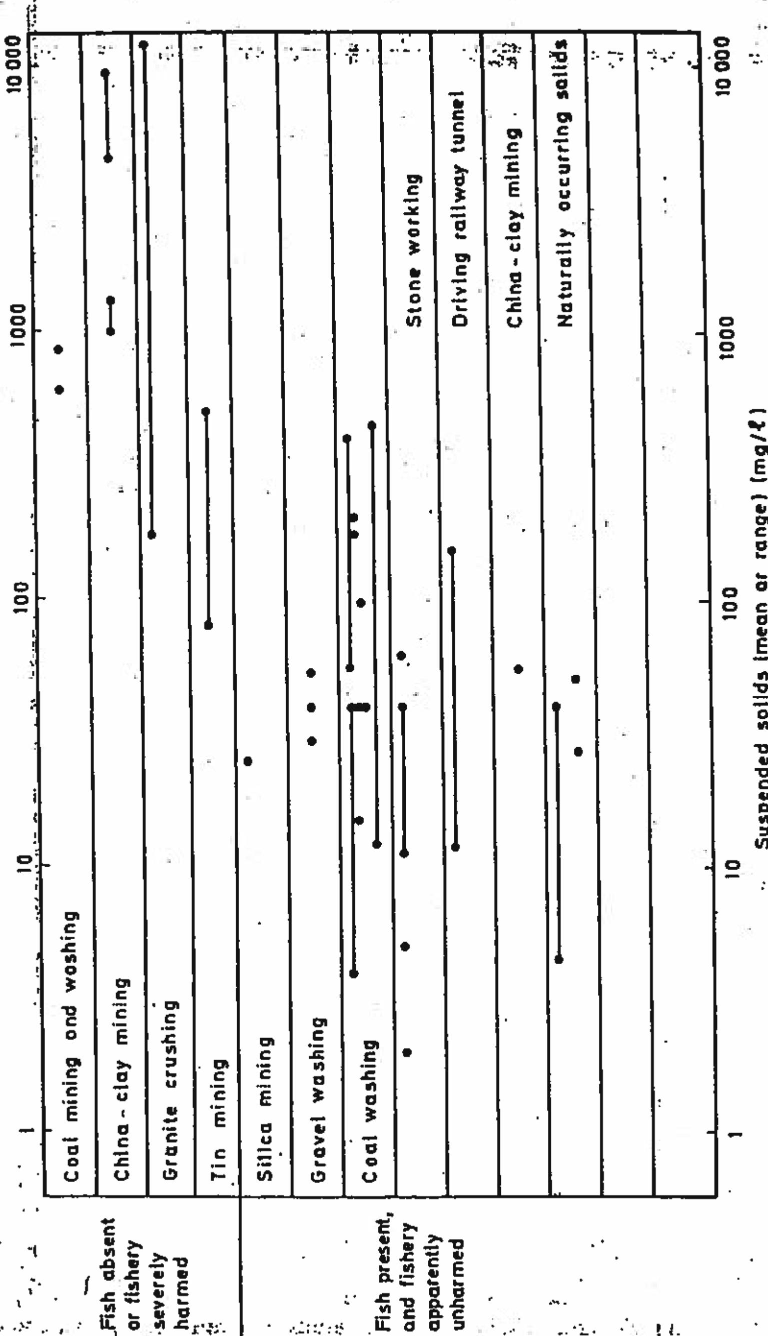

Figure 1.2 Reported status of freshwater fisheries related to the suspended solids content of the water

tion not adversely affected' or 'Fish absent or markedly reduced in abundance'. Care was taken that no data were included if there was reason to suppose that a river was polluted with materials other than inert suspended solids. These data are shown in *Figure 1.2*, together with the information summarized on p. 12, para. 5. Some of the concentrations shown in the figure are means or ranges of a large number of determinations made over a considerable period, whereas some of the others are based on a single observation which may not properly represent the concentrations normally to be found in that stream. However, in spite of this limitation, it may be concluded that nearly all the rivers (or parts of rivers) in which the fisheries were apparently unharmed carried distinctly lower concentrations of suspended solids than those in which the fisheries were either seriously damaged or destroyed. The concentrations in the two categories overlap to some extent and there is not a clearly defined concentration which separates them, but the critical concentration appears to be in the approximate range 100-300 mg/ℓ.

1.4 Tentative water quality criteria for finely divided solid matter

Water quality criteria for suspended solids are needed by those who have to manage inland fisheries and must sometimes decide, for example, how much solid matter could enter a river or lake without undue risk to a fishery, or whether it is worth attempting to develop a commercial or recreational fishery in water already containing a known concentration of such materials. The criteria should therefore be presented in terms of the effect on a fishery which a given concentration of solids is likely to produce.

There is evidence that not all species of fish are equally susceptible to suspended solids, and that not all kinds of solids are equally harmful (p. 5, para. 3). Unfortunately there is very little information on these and many other aspects of the problem, and, as was stated on p. 3, para. 3, much of the evidence which exists is less firmly established than is desirable. The conclusion is that no proposals can be put forward for definite water quality criteria which distinguish between the many different kinds of finely divided solids to which different sorts of inland fisheries may be subjected. Nevertheless, when the evidence is considered as a whole, certain general conclusions can be drawn and some tentative criteria can be based upon them. These are summarized in the following paragraphs, and then are put forward as a basis for discussion and to provide some useful guidance, but it must be emphasized that they are provisional and may well have to be revised when more information becomes available.

The spawning grounds of trout and salmon are very vulnerable to finely divided solids, and quite a small turbidity in the water or deposition of solids on or in the gravel may cause spawning fish to avoid them or prevent successful development of their eggs after they are laid (Section 1.3.2). This may be especially important where a salmon population is restricted by lack of suitable spawning areas.

Except for possible effects on spawning behaviour and egg development and the special case of freshly precipitated iron hydroxide (p. 5, para. 4), there is no evidence that average concentrations less than 25 mg/ℓ have done any harm to fish or fisheries, and there are known to be good fisher[illegible] rivers usually containing about 25 mg/ℓ suspended solids (p. 12, para. 5).

Concentrations above 25 mg/ℓ have reduced the yield of fish from ponds (p. 12, para. 4); 35 mg/ℓ have reduced feeding intensity (p. 8, para. 2); 50 mg/ℓ have reduced the growth rate of trout under laboratory conditions (p. 8, para. 2); 82 mg/ℓ charcoal have killed *Daphnia* (p. 8, para. 5). On the other hand, 85 mg/ℓ is the lowest concentration reported for a stretch of stream containing few or no fish where other factors are satisfactory, and there are many other streams with only slightly lower concentrations where the fishery is not noticeably harmed (p. 12, para. 5 and *Figure 1.2*). In laboratory tests the lowest concentration known to have reduced the expectation of life of fish is 90 mg/ℓ (p. 5, para. 4), and the lowest concentration known to have increased susceptibility to disease is 100 mg/ℓ (p. 6, para. 3).

Some satisfactory fisheries are reported for waters containing 100–400 mg/ℓ suspended solids, but fish are few in number, or absent, in other waters within this range (p. 13, para. 2 and *Figure 1.2*). Similar concentrations of several kinds of solids have also increased susceptibility to disease (p. 6, para. 3), increased mortality rates (p. 4, para. 3), and reduced growth rates (p. 6, para. 2 and p. 12, para. 3). *Daphnia* has been killed by several solids in concentrations within this range (p. 8, para. 5) and, in all the studies considered, the abundance of the invertebrate fauna of stream beds has been drastically reduced (pp. 9, 10).

There is no good evidence that plentiful and varied fish faunas exist in waters normally carrying suspended solids in excess of 400 mg/ℓ although there are streams which carry even 6000 mg/ℓ in which there are very sparse populations of trout (p. 12, para. 5 and *Figure 1.2*). There may be some tolerant species of fish which can provide good fisheries in very muddy waters, but there is no evidence of such fisheries in Europe. An exception is that salmon are netted as they pass through muddy reaches when migrating (p. 7, para. 5).

Many kinds of solids can be present for short periods (possibly up to a few days) in concentrations of at least several thousand mg/ℓ and probably much higher without killing fish, but may damage their gills. This might affect their subsequent survival.

The brief résumé of the evidence on pp. 15, 16 indicates that there is probably no sharply defined concentration of a solid above which fisheries are damaged and below which they are quite unharmed. The impression is rather that any increase in the normally prevailing concentration of suspended matter above quite a low level may cause some decline in the status and value of a freshwater fishery, and that the risk of damage increases with the concentration. However, there is not nearly enough evidence to allow the relation between solids concentration and risk of damage to be defined at all precisely, and the best that can be done at present towards the establishment of water quality criteria for this class of substance is to divide the degree of risk to fisheries into four arbitrarily defined categories and attempt to make rough estimates of the ranges of concentration to which they would generally correspond.

From this approach to the problem the following tentative criteria are presented. With respect to chemically inert solids and to waters which are otherwise satisfactory for the maintenance of freshwater fisheries:

(a) There is no evidence that concentrations of suspended solids less than 25 mg/ℓ have any harmful effects on fisheries.

(b) It should usually be possible to maintain good or moderate fisheries in waters which normally contain 25–80 mg/ℓ suspended solids. Other factors being equal, however, the yield of fish from such waters might be somewhat lower than from those in category (a).

(c) Waters normally containing 80–400 mg/ℓ suspended solids are unlikely to support good freshwater fisheries, although fisheries may sometimes be found at the lower concentrations within this range.

(d) At the best, only poor fisheries are likely to be found in waters which normally contain more than 400 mg/ℓ suspended solids.

In addition, although several thousand mg/ℓ solids may not kill fish during several hours or days exposure, such temporary high concentrations should be prevented in rivers where good fisheries are to be maintained. The spawning grounds of salmon and trout require special consideration and should be kept as free as possible from finely divided solids.

These tentative criteria apply only to chemically inert solids and to waters which are otherwise satisfactory for the maintenance of freshwater fisheries.

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2

EXTREME pH VALUE

Foreword

The preparation of the original report on extreme pH values and inland fisheries was accomplished largely by Mr R. Lloyd who prepared the basic manuscript to be reviewed and supplemented by other members of the Working Party on Water Quality Criteria for European Freshwater Fish as well as a few experts from outside the region, notably Dr P. Doudoroff, Dr W. A. Spoor, and Dr A. Coche.

Subsequently there has been an upsurge of research on the effects of low pH values on fish in connection with three main areas where acid pollution is becoming increasingly recognized as a problem. These areas are:

(a) Lakes and rivers of Central Europe, Southern Scandinavia, and the U.S.A. (the Adirondacks), where acid rainfall is reducing the pH value of the poorly buffered water draining from granite bedrock.

(b) The Appalachian mountain region of the U.S.A. where extensive strip mining for coal has led to increased acid run-off from the exposed rock.

(c) Areas in the vicinity of smelters, particularly in Canada, where again acid rainfall is responsible for reduced pH values in lakes downwind of the chimneys.

Except for the first area, the increasing acidity of the recipient water is accompanied by an increase in the concentration of heavy metals either from leaching or by atmospheric deposition, which may reach concentrations which are themselves harmful to fish populations. Even in Scandinavia, there is evidence that aluminium salts are leached out by acid rainfall. In response to these problems, a considerable number of field and laboratory studies have been carried out using refined techniques.

Much of the recent literature arising from these studies, especially those on acid rainfall, have been reviewed by Schofield (1976), Hendrey *et al.* (1976) and Leivestad *et al.* (1976); also Wright (1975) has published an annotated bibliography. In general, the extra data provided by the studies supports the guidelines laid out in the original report. Therefore, no attempt is made to review all the recent literature, and only a selection of papers which contribute new information is included.

2.1 Summary

In establishing water quality criteria for European inland fisheries, the acidity or alkalinity of the water is an important factor to be considered. There is a normal range of pH values for waters which support a good fishery. A critical review has been made, therefore, of published and unpublished data on both the direct and indirect effects of extreme pH values on fish, with an emphasis on European species; from this review it is clear that the existing data are not sufficiently comprehensive to enable definite pH criteria to be established for each important fish species and for different environmental conditions, but it is thought that sufficient is known for the following general conclusions to be reached.

There is no definite pH range within which a fishery is unharmed and outside which it is damaged, but rather there is a gradual deterioration as the pH values are further removed from the normal range. The pH range which is not directly lethal to fish is 5–9; however, the toxicity of several common pollutants is markedly affected by pH changes within this range, and increasing acidity or alkalinity may make these poisons more toxic. Also, an acid discharge may liberate sufficient carbon dioxide from bicarbonate in the water either to be directly toxic, or to cause the pH range 5–6 to become lethal.

Below a pH value of 5.0, fish mortalities may be expected, although some species may be acclimated to values as low as 3.7. However, the productivity of the aquatic ecosystem is considerably reduced below a pH value of 5.0, so that the yield from a fishery would also become less. Some acid waters may contain precipitated ferric hydroxide which may also act as a lethal factor.

Relatively little is known of the effects of alkaline discharges on a fishery and this may reflect the lesser importance of the problem. Laboratory data show that pH values between 9 and 10 may be harmful to a few species of fish, and above 10 lethal to the remainder. However, where high pH values are caused by the vigorous photosynthetic activity of aquatic plants, accompanying high temperatures and supersaturation of dissolved gases (together with other factors) may also contribute to a greater or lesser extent to fish mortality, making it difficult to correlate mortality with laboratory data on pH value alone.

There are insufficient data to enable even general criteria to be made for other aspects of this problem, such as the avoidance by fish of zones of extreme pH value, or on the growth of fish or their resistance to disease. Research needs are indicated in this chapter.

2.2 Introduction

Because the pH values of a river or lake water can be readily measured in the field with some accuracy, a considerable number of such measurements have been made and the results used in the description of the general character of the water. In an American survey of 409 locations, Ellis (1937) found that the pH range of those containing a good fish population was 6.3–9.0, with the majority of water-courses being within the range 6.7–8.6. This range of natural pH values can be extended beyond the lower limit by the direct discharge of acid effluents or, as a secondary effect, following the flushing of peat bogs by heavy rainfall, or from mine drainage. Rivers and lakes may be made more ...e by either the direct discharge of wastes or as a secondary effect of ...us photosynthetic activity by aquatic plants.

During the past 30 years, reviews of the effect of acids and alkalis on aquatic life have been made by Doudoroff and Katz (1950), Vivier (1954), Marchetti (1962), Jones (1964), and McKee and Woolf (1963). In establishing the water quality criteria for pH values ORSANCO (1955) pointed out that although fish had been found at pH values of 4–10 the safe range was 5–9 and for maximum productivity the pH value should lie between 6.5 and 8.5. These criteria have become widely quoted and the safe range of 5–9 has been accepted and adopted. However, it is not at all certain whether, in field surveys of acid waters, the absence of fish or the presence of a reduced population were caused by the concentration of hydrogen-ions present or by some associated factor such as a lack of chemical nutrients or presence of heavy metals, which may not have been measured. In the same way, fish kills observed in alkaline waters may have been associated with factors other than the concentration of hydroxyl-ions.

It is becoming increasingly clear that no single water quality criterion can be given for a given pollutant irrespective of other environmental variables or factors. Differences in the chemical constituents of the water, and in the sensitivity of various species of fish, may all modify the potential hazard of any given concentration of poison. The purpose of this review is to examine the existing literature on the effect of extreme pH values on fish to see what criteria can be put forward and where further research is necessary. Only the direct or indirect effects of hydrogen and hydroxyl-ions on fish have been reviewed; reference to the effects of those acids such as acetic, benzoic, chromic, or tannic acids, where the anion may be toxic, or alkalis, such as ammonia, where the undissociated molecule is toxic, have not been included. An exception to this has to be made in the case of waters where the low pH value is associated with the presence of humic acids derived from peat; in general, however, the toxicity of such solutions is not dissimilar to those in which the low pH value has been caused by addition of mineral acids and for the purposes of this review it will be assumed that humic acids have a low anionic toxicity.

Prime consideration has been given to literature dealing with species of fish found in Europe, although references to other species are given if they throw additional light on the particular item under discussion. It is thought that most, if not all, of the important published papers on this subject, where relevant to European waters, have been considered in the preparation of this review. Some references have been excluded where the data were incomplete, such as those referring to field observation of mortalities where the pH value of the water is measured some time after the fish were killed. It may also be noted that methods of pH measurement have progressed significantly within the last three decades.

2.3 Literature survey on effects of acid pH values

2.3.1 LABORATORY DATA ON DIRECT LETHAL ACTION

Variables affecting the lethal levels

Concentration of free carbon dioxide The discharge of acid wastes into a water containing bicarbonate alkalinity will result in the formation of free carbon dioxide. If the water is hard, sufficient free carbon dioxide may be liberated to be toxic to fish, even though the pH value does not fall to a ... ormally considered to be lethal (Doudoroff and Katz, 1950). In well aera... aters the toxic levels of free carbon dioxide are usually above 100 mg/ℓ for rainbow trout (*Salmo gairdneri*) (Alabaster, Herbert and Hemens, 1957). However, Lloyd and Jordan (1964) found that much lower levels can considerably reduce the survival times of fish within a range of low pH values which would not otherwise be lethal. In water containing 10 mg/ℓ free carbon dioxide or less, the median lethal pH value for fingerling rainbow trout was 4.5 after 15 days' exposure, but where the water contained more than 20 mg/ℓ free carbon dioxide, the median lethal pH value rose to 5.7; this increased toxicity was apparent only after a day's exposure to the test conditions. It is, therefore, difficult to interpret some published data where the level of free carbon dioxide in the test conditions is either not given or cannot be calculated.

Total hardness, sodium and chloride It has been shown that although survival times of rainbow trout in rapidly lethal pH values become shorter with a decrease in the calcium content of the water, the median lethal levels after 4 days' exposure are 4.18, 4.22, and 4.25 for water of total hardness of 320, 40, and 12 mg/ℓ as $CaCO_3$ respectively (Lloyd and Jordan, 1964). Recent data have shown that at lower concentrations of calcium the toxicity of acid pH values to fish is increased. Bua and Snekvik (1972) showed that for several species of fish, the hatching success at a given pH value was increased with an increase in calcium concentration; also, for brook trout fry (*Salvelinus fontinalis*) at pH 4.0, the percentage survival after 7 days was 0, 10 and 67 at calcium concentrations of 0.2, 1.0 and 2.0 mg Ca/ℓ respectively (C. L. Schofield, personal communication). Recent data show that the toxic effect of acid pH value is enhanced at low concentrations of sodium and chloride; these results are summarized on p. 30, para. 4 and 6.

Size and age of fish In tests using bluegill sunfish (*Lepomis macrochirus*) of different size groups, Cairns and Scheier (1958) found that the median lethal pH values for four days exposure were 3.6, 3.6, and 3.5 for fish with mean lengths of 3.9, 6.7, and 14.2 cm respectively. Lloyd and Jordan (1964) found no correlation between sensitivity and the size of rainbow trout of any one age group, but a positive correlation existed between age and sensitivity; 16-month old fish survived more than three times as long as those four months old, although the increase in resistance, in terms of lethal pH value for these two age groups, was only 0.3 of a pH unit.

There is increasing evidence that the young stages of the life cycle are more sensitive than the adult fish. The viability of roach (*Rutilus rutilus*) and perch (*Perca fluviatilis*) eggs kept in natural lake waters with a range of acidities was reduced below pH values of 5.5 and 4.7 respectively (Milbrink and Johansson, 1975) (cf. p. 26, para. 3; p. 27); these authors refer to similar work with pike (*Esox lucius*) which gave a corresponding value of 5.0 (cf. p. 27, para. 3). Kwain (1975) found that no rainbow trout eggs survived at pH values of less than 4.5, but that there was a reasonable survival above pH 5.0; yearling rainbow trout were more resistant to acid pH values than were fingerlings. Menendez (1976) found reduced viability of eggs of brook trout at pH values below 5.1, with alevin mortalities occurring below 6.0; however adult mortalities only occurred below 4.5 [illegible]

Acclimation pH value Although in early literature, it was stated that fish could not withstand sudden changes in pH value, both Brown and Jewell (1926) and Wiebe (1931) found that various North American coarse fish species could withstand rapid transfer between waters of widely different pH values within the normal range. Lloyd and Jordan (1964) found no difference between the susceptibility of batches of rainbow trout acclimated to pH values of 8.40, 7.50, and 6.55 when they were exposed to lethal acid solutions. Falk and Dunson (1977) found that short-term (2–24 h) acclimation to low non-lethal pH values in the range 4–6 did not significantly increase the survival times of brook trout in acutely lethal acid solutions, thus confirming earlier work. However, Trojnar (1977) raised brook trout in waters of pH values 4.65, 4.97 and 8.07 in which survival to hatching was 76.4, 84.2 and 91.1 per cent respectively and, when the fry raised for 78 days at pH values of 4.65, 5.64 and 8.07 were exposed to a pH value of 4.0, 76 per cent of those raised in acid waters survived, whereas all those raised in alkaline waters died. This is in agreement with general Swedish experience in stocking acid lakes with non-acclimated yearling salmonids (M. Grande, personal communication). Although acclimation pH values within the normal range may, therefore, be discounted when comparing the results of toxicity tests, it would be incorrect to assume on this evidence that fish might not be able to acclimate or acclimatize slowly to a progressive decrease in the pH value of the water towards that normally considered to be lethal.

There is some evidence that strains of salmonid species may differ in their resistance to low pH values. Gjvedrem (1976) collected 77 different strains of brown trout from acid waters in Norway, bred them, and found a considerable variation between the resistance of the eggs and alevins to pH values of 4.7 and 5.2. Similar studies with inbred strains of brook trout (Robinson *et al.*, 1976) also demonstrated the possibility of inherited acid tolerance even among fish which had not been selected from acid waters. Therefore, some acclimation to low pH values may occur in the juvenile stages of fish, and there may be some selection in acid-polluted waters for strains which have an inherited resistance to these conditions.

Time of year Sexually mature brook trout were most sensitive to acid pH values in the summer (Dively *et al.*, 1977) although data obtained by Robinson *et al.* (1976) and Falk and Dunson (1977) showed the opposite to be true for immature brook trout.

Other factors There are no reliable data for the effect of low dissolved oxygen concentration on lethal acid pH values. Kwain (1975) found that rainbow trout embryos were more sensitive to sulphuric acid at 5 °C than at 10 °C, the median lethal pH values being 5.52 and 4.75 respectively.

Summary of toxicity data

Salmonids Bishai (1960) found that for young Atlantic salmon (*Salmo salar*), and for sea trout and brown trout (*Salmo trutta*), the lethal pH value was 5.8–6.2 in 2-day tests, but since the water was acidified with free carbon dioxide, it is not clear whether dissolved carbon dioxide or hydrogen-ion concentration was the main toxic agent. Dahl (1927), using water acidified with peat, found that 80 per cent of trout in the yolk sac stage died within 20 days at pH values of 4.7-5.4, and 10 per cent died in the range 5.1-5.7. Salmon in the yolk sac stage held in dilutions of peaty waters were found to have a median lethal pH value of 4.5 at 12 days; also, yearling brown trout taken from a soft acid river (pH 5.85) died within 12-14 h at a pH value of 3.3 and survived a pH value of 4.1 for 7 days (M. Grande, personal communication). Lloyd and Jordan (1964), using hydrochloric acid, found that in water of low carbon dioxide content, the median lethal pH for a 15-day exposure was 4.5 for fingerling rainbow trout. This suggests that the brown trout were more resistant than rainbow trout and, even allowing for the larger size, there is a possibility that these fish were acclimated to some extent to the acid environment. Carter (1964), using a continuous-flow apparatus and acidifying 50 per cent sea water with either hydrochloric or sulphuric acid, and without subsequent aeration, found that the median periods of survival of fingerling brown trout at pH values of 4.5 and 4.6 were 61 and 42 h respectively; however, it is possible that more than 20 mg/ℓ free carbon dioxide was present under these test conditions, and, if so, the results would agree with those of Lloyd and Jordan (1964) for rainbow trout.

M. Grande (personal communication) found that the hatching success of salmon eggs in a water acidified with sulphuric acid to give a pH value of 4.59 was 96 per cent compared with only 48 per cent at a pH value of 4.34; moreover, only 50 per cent of eyed-ova of brown trout hatched in a solution acidified with peaty water to give a pH value of 4.77. No mortalities were observed among trout eggs or alevins (species not given) exposed to water acidified with hydrochloric acid in which pH values fluctuated between 4 and 5 (Krishna, 1953) whereas mortalities occurred below a pH value of 4, but neither the duration of the experiment, nor the concentration of free carbon dioxide, are given.

Other species Using a soft water acidified with nitric acid, Carpenter (1927) found that the survival time of minnow (*Phoxinus phoxinus*) was 28 h at pH 5.0, whereas a pH value of 5.2 had no effect in three days. Under similar conditions, but using hydrochloric acid, stickleback (*Gasterosteus aculeatus*) survived for about 5½ days at pH 4.8 and lived for as long as the control fish (10 days) at pH 5.0 (Jones, 1939). However, the mortality of control fish detracts from these results, and the true lethal limit of pH value may be slightly lower.

Although roach were found to have shorter survival times than rainbow trout in solutions with pH values between 3.0 and 4.1 (Lloyd and Jordan, 1964), the 8-day median lethal pH value was 4.2 for both species. Ellis (1937) found that the 96-hour median lethal pH value for goldfish (*Carassius auratus*) in a hard water acidified with sulphuric acid was 4.0, compared with 4.3 in a soft water and 4.5 for hydrochloric acid in a hard water; it is doubtful whether the differences between these values are of any significance and furthermore the concentration of free carbon dioxide cannot be calculated. A pH value of 4.5, using sulphuric acid, was said to be detrimental to goldfish over a period of two weeks. Lewis and Peters (1956) found that 35-mm common carp (*Cyprinus carpio*) were killed within 4 h at a pH value of 4.9, but the level of dissolved oxygen was low (2.4 mg/ℓ) and the experimental technique almost certainly led to a high level of free carbon dioxide and freshly precipitated ferric hydroxide. Briuchanova (1937) reports a threshold pH value of 5.0 for carp compared with 4.0 for the ...ian carp (*Carassius carassius*).

...lodin (1960) showed that the resistance of the various developmenta[l]

stages of burbot (*Lota lota*) embryos to acid water varied, and successful development could take place only within a narrow pH range. The most sensitive stage was that of embryo segmentation at which a pH value of 6.0 was the critical lower level, but during subsequent development the critical level lowered to 5.0. Dyk and Lucky (1956) found that the period of motility of carp sperm was reduced in water acidified with peat to a pH value of 6.5; Elster and Mann (1950) demonstrated a decreased motility of carp sperm at pH 4.5, and lower pH values were lethal to them.

2.3.2 FIELD OBSERVATIONS

Natural populations Natural populations of brown trout have been found in waters of pH value as low as 4.5 (Menzies, 1927) and 4.9 (Campbell, 1961). Creaser (1930) reported that the brook trout was found in waters with a pH value of 4.1. Results of a survey of fish populations (mainly brown trout) in 1679 lakes in Norway have been summarized by Leivestad *et al.* (1976); few fishless lakes are found with a pH value above 5.5, although a few lakes within the range 4.5-4.7 contain good fisheries. In acid rivers, salmon are reported to be the first species to disappear, with sea-trout and brown trout showing higher resistance. In lakes, perch and eel (*Anguilla anguilla*) appear to be the most resistant species. Similar phased reductions in fish species have been found by Beamish (1974) in acid-polluted lakes in Ontario, where lake trout (*Salvelinus namaycush*) and small-mouth bass (*Micropterus dolomieui*) are the most sensitive and yellow perch (*Perca flavescens*) the most resistant, although the presence of heavy metals may contribute to these findings. From a survey of acid lakes in Sweden, Almer *et al.* (1974) concluded that the reproduction of roach was affected at pH values below 5.5; the associated calcium and conductivity data are not quoted. Surveys of acid Norwegian lakes have confirmed that where low concentrations of calcium are present, self-sustaining brown trout populations are less likely to be present than in similar acid lakes with higher calcium concentrations (Wright and Snekvik, 1978).

Vallin (1953) reports that in L. Blamisus (northern Sweden) the water has a pH value of 2.8-3.1 and an iron content of 6-7 mg Fe/ℓ in the surface waters; the flora and fauna are poor and no fish have been reported there. The water from this lake flows into L. Sladen which has a pH value of 3.7-3.8, an iron content of 0.3-1.2 mg Fe/ℓ, and a slightly more abundant flora and fauna including roach, perch and pike together with bream (*Abramis brama*) during the breeding season. However, in the spring, the pH falls to 3.5-3.7 and some local fish kills of roach have been observed. It is evident that these roach can survive at lower pH values than those found to be lethal in laboratory experiments (p. 25, para. 5) and it is possible that some long-term acclimation has taken place. In L. Sysmajarvi (Finland) Ryhanen (1961) reported that, during summer, the pH value ranged from 3.5 at the outlet of an acid stream to 4.6, with a large zone which had a pH value of 4.2-4.4. Bream, perch, roach and pike were present, but only pike were able to breed in the large zone where the pH values were between 4.2 and 4.4. No under-yearlings of bream, perch or roach were present and the older fish presumably migrated from the more alkaline streams feeding the lake. Dyk (1940) states that tench (*Tinca tinca*) can be kept for two weeks in a water of pH 3.6-3.8 without adverse effect, although these values adversely affect carp.

Although there are several field studies published on the [...]ulation of

American waters polluted by strip-mining activities, the results are difficult to interpret since high hydrogen-ion concentrations are associated with high heavy metal content. A comprehensive survey of six lakes with pH ranges between 2.5–3.2 and 7.4–8.2 has been made by Smith and Frey (1971). The two most acid lakes (pH ranges of surface water of 2.5–3.2 and 3.0–3.4 respectively) were fishless but green sunfish (*Lepomis cyanellus*) only were caught in a lake with a surface pH range of 3.6–6.4; five species of fish were present in a lake with a surface pH range of 4.5–7.6. However, the two most acid lakes contained 2.9 and 0.8 mg Zn/ℓ and 82 and 4.7 mg Fe/ℓ respectively.

A survey of the acid lakes in the vicinity of Sudbury, Ontario, has been made by Beamish (1976); some sensitive species of fish declined in numbers as the pH fell below 6.0, but increasing acidity was accompanied by increased contamination by heavy metals, which may have contributed to the toxicity of the water. Although this was held not to be the case, the data on heavy metal toxicity used for the comparison were for other species of fish and in water of different chemical characteristics.

It is becoming clear that it is not possible to give precise limits of pH value above which a good population of a fish species would be expected. Genetically determined differences between strains of species, selection and acclimation may affect the sensitivity of the fish, and low concentrations of sodium, calcium, and chloride may decrease their ability to osmoregulate (p. 29, para. 6). Data from chronic tests carried out in the laboratory may tend to overestimate the long-term effects of acid pH values on natural fish populations, for example, through not having taken into account the influence of minor components in the water.

Fish kills Fish kills occur with two main types of acid pollution. Heavy rainfall may flush out peat bogs or strip mining areas and produce a sudden flush of acid water, or acid discharges from industrial sources may temporarily lower the pH value of the water to a lethal level. In both cases, the pH value of the water is usually measured after the fish kill has occurred and, therefore, the figures may bear little relation to the pH values which were actually responsible for the mortality.

The position is further complicated in that these acid run-offs can contain considerable quantities of dissolved ferric sulphate which may become hydrolysed at pH values above 3.0 to form ferric hydroxide (Dahl, J., 1963), a process which might be accelerated by the presence of *Thiobacillus* species (Fjerdingstad, 1958; Dahl, J., 1963). Roach which have been killed in such waters have had brown deposits on their gills (Vallin, 1953). Schiemenz (1937) states that pH values below 5.4 are dangerous to common carp and tench, but a water containing much iron is dangerous at a pH value of 5.4. Haupt (1932) found that one-year-old carp died within five days in a water of pH 4.3–4.4 containing 1.2–10.5 mg Fe/ℓ. Larsen and Olsen (1948) found that fish kills occurred in a trout hatchery when the pH value of the water was 6.2–7.0 and the water contained 1.5–20 mg Fe/ℓ; the cause of death was attributed to the precipitation of ferric hydroxide on the gills, since the pH value of the water was higher than the lethal value. In laboratory experiments, Jones (1939) found that the toxicity of solutions of ferric chloride in soft water could be wholly accounted for by the low pH value, and he concluded that ferric salts had a very low toxicity. However, only 1 mg Fe/ℓ was required to give the threshold pH value of 5.0 with the dilution water used, and it is possible that this concentration was too low to have a toxic action if precipitated. If fish are killed by ferric hydroxide in suspension, the concentrations which appear to be lethal are lower than that found for inert suspended material (Chapter 1), but the presence of the precipitate on the gills of dead fish does not necessarily indicate that this was the primary cause of death. Lewis and Peters (1956), using green sunfish and largemouth bass, found that high concentrations of precipitated ferric hydroxide (up to 27 mg Fe/ℓ) had no effect on these fish in acid waters during a two- or three-day test in which the pH values varied within the range 3.7–4.7.

Recent experiments by Decker and Menendez (1974) showed that the 96-h LC50 for iron to brook trout was 1.75 mg/ℓ at pH 7.0, 0.48 at pH 6.0 and 0.41 at pH 5.5; a constant-flow experimental technique was used which ensured that a continuous supply of freshly-precipitated iron hydroxide was brought into contact with the test fish. However, Sykora *et al.* (1975) found that the maximum level which allowed the normal survival and growth of brook trout was 7.5–12.5 mg/ℓ; in these experiments a 1½-h delay tank was introduced to ensure the oxidation of ferrous hydroxide to the ferric state. It is possible that experimental techniques which can affect the particle size and chemical nature of the suspension may exert a considerable influence on the results. Smith, Sykora and Shapiro (1973) found that fathead minnow were more sensitive, with hatchability and growth being reduced at the lowest concentration tested, 1.5 mg Fe/ℓ.

Surber (1935) found that after rainbow trout were transferred from water with a pH value of 7.1 to a soft hatchery water of pH 5.4, 35 per cent of them died. Lloyd and Jordan (1964) point out that the water was probably high in free carbon dioxide (about 40 mg/ℓ) and the observed mortalities were similar to those which would be predicted for these conditions from their laboratory data, and therefore the mortality was not caused simply by the change in pH value alone.

Vallin (1962) stated that when the R. Morrumsan in southern Sweden (pH value 6.0) was polluted by an increased discharge from a sulphite cellulose factory, the pH value fell to 4.0–4.5 and mortalities of tench, roach and bream were recorded, whereas perch and pike were more resistant. Neutralization of the effluent with lime raised the pH value to above 5.0 and further fish kills were avoided, so that it is very likely that this effect was caused either directly or indirectly by the concentration of hydrogen-ions in the water.

In the cases where the toxicity was not complicated by the presence of ferric salts, the data on fish kills are in reasonable agreement with the results of laboratory experiments.

2.3.3 MODE OF TOXIC ACTION

The toxic action of hydrogen-ions on goldfish has been ascribed by several authors to the precipitation of mucus on the gill epithelium causing death by suffocation, or by precipitation of proteins within the epithelial cells (Ellis, 1937; Westfall, 1945). Kuhn and Koecke (1956), using solutions of hydrochloric and sulphuric acids in distilled water, found that the exposure of goldfish for one hour to a pH value of 4.0 led to complete destruction of the gill epithelium, a rather rapid degeneration since this pH value has been found to be the 4-day median tolerance limit (Ellis, 1937).

Lloyd and Jordan (1964) found no evidence of gill tissue damage or precipitated mucus in rainbow trout taken at death after a 7½-h exposure to a solution of pH value 3.4. Histopathological studies by Daye and Garside (1976) on surficial tissues of brook trout exposed for up to 7 days to a range of pH values above 2.2 showed that the gills were the most sensitive, with hypertrophy of the mucus cells at the base of the filaments at pH 5.2 and accumulation of mucus on the gills of surviving fish. In acutely lethal solutions the gill epithelium became detached from the pilaster cells. The lethal pH limit for this species for a 7-day exposure period was 3.5 (Daye and Garside, 1975). Dively *et al.* (1977) also noted that mucus accumulated on the gills of brook trout in acid solutions when respiratory distress was at a maximum.

Dahl, K. (1927) found that salmon held at a pH value of 4.7–5.4 (which had killed 80 per cent of them in 17 days) recovered on transfer to clean water (pH value 6.4). Lloyd and Jordan (1964) found that rainbow trout which had overturned after 24 h in a solution of pH value 3.8, recovered on transfer to clean water at pH 8.2. It would appear, therefore, that salmonids do not suffer any permanent damage from exposure to acid solutions for periods of time too short to cause death. The pH value of the venous blood of rainbow trout killed by highly acid water (pH value 3.15) was 0.2 units lower than that of control fish in water where little free carbon dioxide was present, and 0.55 units lower in fish dying in water of pH value 4.50 and containing 50 mg/ℓ free carbon dioxide (Lloyd and Jordan, 1964). These authors were of the opinion that, in the rainbow trout, the cause of death is acidaemia.

Dively *et al.* (1977) found an increase in the P_{CO_2} of arterial blood of brook trout, and also increases in gill ventilation rate, haematocrit and activity when the fish were exposed to a pH value of 4.2; little change occurred in the blood pH value. They also found a reduction in serum sodium content, which agrees with the findings of Packer and Dunson (1970, 1972) for this species. Leivestad and Muniz (1976) found that brown trout dying in an acid Norwegian river (pH value approx. 5.2) had low plasma sodium and chloride concentrations (but normal P_{CO_2} and haematocrit) and suggest that inability to osmoregulate is a major cause of mortality. Addition of sodium chloride to snow melt water containing 1.65 mg Na/ℓ to raise the sodium content to 14.4 mg/ℓ increased the survival of brown trout alevins from 30 per cent to 83 per cent at a pH value of 4.9; similar results were obtained with salmon, sea-trout and Arctic char (*Salvelinus alpinus*) (Bua and Snekvik, 1972, quoted in Leivestad *et al.*, 1976). Packer and Dunson (1970) also found that increasing the sodium content of the water prolonged the survival of brook trout exposed to acute lethal pH values; at death the sodium concentration in the blood plasma was normal and it is likely that death was caused by other factors. In other tests at a pH value of 3.0, the blood pH value was reduced by 0.44 units within a 1½-h exposure period.

The influence of acidity on the sodium balance of brown trout has been studied using radio-tracers (P. G. McWilliams and W. T. W. Potts, personal communication). At pH levels greater than 5.0, influx and outflux are approximately equal and body sodium is maintained; below pH 5.0 the influx is increasingly reduced, and the efflux is increased. While the influx is most sensitive to acid pH values, the efflux is more responsive to the calcium concentration of the water; it is thought that lack of calcium increases cell membrane permeability. Brown trout of different strains and different acclimation histories have different sodium exchange rates and so react differently to acid stress. Transfer of these fish to a more acid water produces an initial reduction in sodium uptake followed by an increased level within 1–2 days.

It seems that the prime mode of toxic action is still unresolved; disruption of the gill epithelium, production of mucus on gills, inability to osmoregulate and acidosis of the blood have all been found to be associated with harmful acid pH values.

There are few data on the sublethal effects of hydrogen-ion toxicity; Neess (1949) states that below a pH value of 5.5, carp develop a hypersensitivity to bacteria, and it is commonly believed in fish farming practice that a low pH value increases the susceptibility of fish to disease. It is quite possible that fish weakened by acid pH values may be more susceptible to disease, but there are no controlled laboratory experiments known to us which demonstrate this effect. In the case of field observations, it is difficult to separate pH value from other associated environmental variables, including water hardness, which may also be of importance.

The life cycles of some fish parasites are affected by pH value. *Ichthyophthirus* can reproduce normally within the pH range 7.2–8.7, and can become attached to the host fish only within the range 5.5–10.1; on the other hand, both *Costria necatrix* and *Chilodonella* require an acid environment for reproduction (Bauer, 1959). Frost (1939) found no difference between the incidence of parasites in a natural population of trout living in water at a pH value of 5.6 and those at a pH value of 7.8–8.0.

2.3.4 AVOIDANCE REACTIONS

Several authors have measured the ability of fish to detect and avoid acid pH levels under laboratory conditions. In some of these experiments it is difficult to judge whether the fish were detecting changes in hydrogen-ion concentration or differences in the level of free carbon dioxide.

Jones (1948) found that stickleback definitely avoided acid waters with pH values of up to 5.4, which was slightly above the lethal level of 4.8–5.0, and showed a very vague negative reaction to a pH value of 5.8, when the alternative choice was water with a pH value of 6.8. Ishio (1965) found that carp and goldfish avoided pH values in the range 5.5–7.0, with preference values of 8.4 and 7.2 respectively. Höglund (1961) separated the effects of free carbon dioxide from that of hydrogen-ion concentration and showed that roach tend to avoid pH values below 5.6 and salmon parr pH values below 5.3.

Höglund also found that pH values in the range 5.6–10.5 were non-directive for roach, and that the range 5.3 to at least 7.4 was non-directive for salmon parr. Brown and Jewell (1926), using populations of fish from an acid lake (pH values 6.4–6.6) and from an alkaline lake (pH values 8.4–8.6) found that, in a gradient tank where there was a choice between these two waters, the fish from the acid lake preferred the acid water and those from the alkaline lake the alkaline water. It is not established, however, that the fish were reacting to pH *per se*.

In the discussion to Ishio's paper (1965), Doudoroff questioned the ecological significance of experiments in which fish were exposed to steep [illegible]ntration gradients of substances, and thought that reactions in the field, where changes in concentration occurred either over a longer distance or during a longer period of time, might well be different since progressive adaptation to the changing conditions might occur.

There are no accurate field data to suggest that fish migrate to an area of optimum hydrogen-ion concentration. The fact that various species of fish have been observed at pH values considerably lower than 5.0 indicates that laboratory tests demonstrate only the ability of fish to detect changes in the pH value of the water, and it does not necessarily follow that changes will be avoided in the field where the fish are also exposed to other, perhaps more powerful, stimuli. Although there are reports of fish moving downstream when an acid flush lowered the pH value of the water (Högbom, 1921; Parsons, 1952), there are no data on the pH value to which these were acclimated, nor on the acidity required to initiate movement.

2.3.5 EFFECT ON GROWTH

It is well known that the growth rate of fish in acid waters is usually less than that under alkaline conditions. Frost (1939) came to the conclusion that some factor other than the amount of food available was responsible for the lower growth rates of trout in the acid head waters of the R. Liffey compared with alkaline reaches further downstream. Campbell (1961) found that there was no correlation between pH value and growth rate of brown trout in nine lakes with pH values ranging from 4.9 to 8.4; however, he suggested that in some acid lakes, where there were ample spawning grounds, the slow growth rates were due to a too high population density for the available food supply. In an acid lake with no natural spawning grounds, the growth rate of trout artificially stocked at a low density was equal to that of fish in alkaline lakes. A similar observation was made by Pentelow (1944). From data supplied by the Department of Agriculture and Fisheries of Eire (E. Twomey, personal communication), the growth rate of brown trout in Irish rivers and lakes was generally higher in alkaline waters, but the best growth rate recorded was in a lake with a pH value of 5.4.

Experiments have now been carried out on the growth rate of fish kept at different pH values and fed the same ration. No difference was found in the growth rate of 18-month-old brown trout kept at pH values 6.26, 5.44 and 5.00 and fed with a daily ration of 2.9 per cent of initial body weight (Jacobsen, 1977). However, Menendez (1976) found that brook trout grew more slowly at pH values of 5.0–6.5 compared with that of the controls, although growth rates after ten weeks exposure appeared to be similar. Muniz and Leivestad (quoted in Leivestad *et al.*, 1976) also found that brook trout grew more slowly in an acid water (pH value 4.2–5.0) over a period of a year, compared with fish kept in the same water supply but neutralized with calcium carbonate to give a pH value of 5.2–6.5. It is not clear whether these apparently contradictory results are due to species difference or to the experimental techniques used. However, Leivestad *et al.* (1976) also quote Scandinavian studies which indicate that acidification of waters can initially increase growth rate of fish because of reduced competition for food.

Bruchanova (1937) found that crucian carp and common carp appeared to feed normally over the tolerated pH range, but that maximum growth was achieved at a pH value of 5.5 for crucian carp and 6.0–6.2 for common carp. In northern Germany the optimum pH range for carp growth was 6.8–7.5; below pH 6.0 the growth rate is reduced, and this is associated with a reduced food supply (H. Mann, personal communication). Parsons (1952) reports 'amazing growth' of bluegill sunfish in a pool at a pH value of 4.5.

The relation between growth rate and hydrogen-ion concentration is unclear, and it is possible that other ions present, such as sodium, calcium, and chloride, may exert a modifying effect.

2.3.6 EFFECT ON FOOD SUPPLY

A major factor in the poor productivity of naturally acid waters is the low concentration of dissolved mineral nutrients entering the ecosystem from surface drainage. It has been estimated that in Belgium, the productivity of ponds is three times greater in the alkaline areas (pH values 7.0–7.5) than in the acid areas (pH values 5.0–5.6) but the difference between the productivity of rivers in these areas is not so great (Huet, 1941).

However, there are several references suggesting that low pH values resulting from pollution affect the recirculation of nutrients in the aquatic ecosystem by reducing the rate of decomposition of organic matter and by inhibiting nitrogen fixation (Neess, 1949; ORSANCO, 1955). Harrison (1956) found that acid pollution from gold mining in South Africa produced typical peat bog conditions, with large accumulations of undecayed plant debris, in a stream with a pH range of 3.7–4.8. It is a common fish culture practice to add calcium carbonate to ponds where the pH value of the water or pond bottom is too low.

Certain species of invertebrates can withstand very high hydrogen-ion concentrations. Lackey (1938) found *Gammarus* species in two streams with pH values of 2.2 and 3.2 respectively; mosquito larvae in a stream at pH 2.3, and caddis larvae (Trichoptera) at pH 2.4. He points out that a wide variety of different species of animals and plants does not occur in waters with pH values below 6.2 but that large numbers of some species may occur in highly acid waters. Harrison (1956) found that species common to alkaline or neutral waters were found at pH values down to 4.0, but a specialized flora and fauna developed below 5.0 to at least as low as 2.9; Robeck (1965) reports six genera of caddis from water of pH value 3.0. Since these lower pH values are well below those lethal to fish, it would seem that absence of invertebrates is unlikely to be a limiting factor for fish in acid waters. Although *Gammarus* is frequently absent from acid streams, this may be correlated with low calcium content, dissolved oxygen distribution or current speed, rather than hydrogen-ion content (Huet, 1941).

There have been no data published since 1969 which indicate that lack of food organisms may be a limiting factor for fish populations in acid waters (except where precipitated iron salts are present) although the number of species present and the productivity of the water may be reduced; recent Scandinavian data have been reviewed by Hendry *et al.* (1976). Also, Tomkiewicz and Dunson (1977) concluded that sufficient fish food organisms were present in a stream at pH 4.5–5.0 to support a limited population of fish.

2.3.7 TOXICITY OF OTHER POISONS

A change in the pH value of the water following the discharge of an acid effluent may modify the toxicity of other poisons already present, particularly those which dissociate into an ionized and an un-ionized fraction of which one is markedly toxic. A classic example is the nickelocyanide complex which is 500 times more toxic at pH 7.0 than at 8.0 (Doudoroff, 1956) because the complex dissociates into cyanide and nickel ions and a proportion of the cyanide forms the highly toxic undissociated HCN. Conversely, ammonia is almost one tenth as toxic at pH 7.0 as at 8.0 (Wuhrmann and Woker, 1948). Other substances whose toxicities are affected by the pH value of the water are cyanide alone (Wuhrmann and Woker, 1948) and sodium sulphide (Longwell and Pentelow, 1935; Bonn and Follis, 1967). Recently, Mount (1966) has shown that the toxicity of zinc to fathead minnows (*Pimephales promelas*) decreases with a fall in pH value from 8.6 to 6.0 (the 4-day median lethal concentration (LC50) being 6.4 and 21.8 mg Zn/ℓ respectively in water of total hardness of 100 mg/ℓ as $CaCO_3$) but there was no further decrease in toxicity when the pH value was reduced further to 5.0. There are other poisons, the toxicities of which are affected by pH changes, but these cannot be considered here.

Poisons which are known to be not affected by changes in pH value of the water within the normal range include ABS (Marchetti, 1966) and gas-liquor phenols (Herbert, 1962).

The discharge of acids to water with a high bicarbonate alkalinity will liberate free carbon dioxide in concentrations high enough to be directly lethal to fish, even though the pH value of the water does not fall to a level considered to be harmful (Doudoroff and Katz, 1950). Sublethal levels of free carbon dioxide may increase the sensitivity of fish to low levels of dissolved oxygen (Alabaster, Herbert and Hemens, 1957) unless given prior acclimation (Doudoroff and Warren, 1965). It is not known whether sudden exposure to high but sublethal levels of free carbon dioxide increases the sensitivity of fish to other dissolved poisons.

Although there is reasonable agreement between laboratory data and field observations of fish kills, there is good evidence that some fish populations can tolerate pH levels lower than those which would be considered lethal from these studies. Moreover, this also indicates that such acid conditions are not necessarily actively avoided. In general, coarse fish appear to be at least as resistant as salmonid species to acid pollution and some species may be more resistant. However, a chronic acid discharge which lowers the pH value of a river or lake to below 5.0 will reduce the primary productivity and therefore the food supply, so that if fish are still present, either their numbers or their growth rate will be reduced. A more detailed summary of the data is given at the end of this review in *Table 2.1*.

There is considerable scope for further research in this field. There is conflicting evidence on the effect of iron salts on fish in acid waters; the presence of soluble iron salts does not appear to harm fish but the precipitated hydroxide may be more toxic than would be expected from studies on other suspended solids. There is little information on the relation between pH value and the resistance of fish to disease, or on their growth rate, or food/body-weight conversion ratios.

2.4 Literature survey on effects on alkaline pH values

2.4.1 LABORATORY DATA ON DIRECT LETHAL ACTION

Variables affecting the lethal levels

Effect of size Using sodium hydroxide, Cairns and Scheier (1958) found that the 4-day median tolerance limits of pH value for bluegill sunfish were 10.5, 10.5 and 9.9 for fish with mean lengths of 39, 61, and 142 mm respectively, showing that susceptibility increases with size. Bandt (1936), however, states that the median tolerance levels of alkaline pH values are 0.2 units higher for large fish and Mantelman (1967) has shown that the resistance of *Coregonus peled* and common carp increases with age.

Acclimation pH value Jordan and Lloyd (1964) showed that although the acclimation pH value had no effect on the resistance of rainbow trout to pH values high enough to kill in a few hours, the 1-day median lethal values were 9.86, 9.91 and 10.13 for batches acclimated to pH values of 6.55, 7.50 and 8.40 respectively, and that this difference, although small, was statistically significant.

Dissolved oxygen concentration (DO) There are no accurate data on the effect of high pH values on fish at different levels of dissolved oxygen, although this might be important since alkaline conditions following from intense photosynthetic activity of aquatic plants are normally accompanied by high levels of dissolved oxygen. Wiebe (1931) found that bluegill sunfish showed distress, and some died, in water of pH value 9.6 and a DO of 5 mg/ℓ, but were unaffected by a pH value of 9.5 and a DO of 10 mg/ℓ. If the toxicity of an alkaline solution is related to the pH value at the gill surface and not to the pH value of the bulk of the solution, then an increase in DO in the water may lead to an increased concentration of excreted free carbon dioxide at the gill surface (Lloyd, 1961) and therefore to a lower pH value there. The extent to which the pH value at the gill surface is changed would also depend in part on the buffering capacity of the water; none of these factors has been the subject of controlled experimentation.

Other factors There are no data for the effect of temperature, or water hardness, on the toxicity of hydroxyl-ion concentrations.

Summary of toxicity data

Salmonids In tests using concrete blocks as a source of alkali, Bandt (1936) found that the minimum lethal pH value for trout was 9.2. This is slightly lower than the values found for rainbow trout by Jordan and Lloyd (1964) who found that the median lethal pH value for a 15-day exposure was 9.5; but the difference between these results may be that between the minimum values, which presumably killed no fish, and the median values which k[illegible]d 50 per cent of a batch. Sprague (1964) reports that only 5 per cent of a batch of 40 yearling Atlantic salmon died within six weeks when kept in a water supply carried through asbestos-cement pipelines and having a pH value of 9.5. Carter (1964) acclimated brown trout to full strength sea water and exposed them to alkaline saline solution; a pH value of 9.6 gave a median lethal period of 20 h, whereas fish at a pH value of 9.5 survived for more than four days. Survival times of these fish in lethal alkaline solutions were considerably less than that for rainbow trout in fresh water at similar pH values (Jordan and Lloyd, 1964). Rosseland (1956) reports that an alkaline effluent was toxic to young salmon and brown trout, a pH value of 9.7 being lethal within a day; whereas none died during $1\frac{1}{2}$ days at pH 9.0. Long-term experiments with young stages of *Coregonus peled* showed that the highest safe pH value was 8.6–9.2 (Mantelman, 1967).

Krishna (1953) found that with eggs and alevins of trout, mortalities occurred above a pH value of 9.0, but the period of exposure is not given.

Other species Bandt (1936), in experiments similar to that on p. 35, para. 5, found that the minimum lethal value for perch was 9.2, roach 10.4, carp 10.8, pike 10.7, and tench 10.8. Jordan and Lloyd (1964) found that the median lethal pH value for a 10-day exposure was 10.15 for roach, slightly less than that given by Bandt, and Mantelman (1967) gives the highest safe concentration for common carp as 9.2–9.6. Sanborn (1945), using sodium hydroxide, found that goldfish died within 3–20 h at a pH value of 10.9, and lived for more than seven days at a value of 10.4. Experiments using sodium carbonate and calcium hydroxide gave similar results, so that these cations appear to have no effect on the toxicity of the hydroxyl-ions. Rosseland (1956) found that minnow were slightly more sensitive than brown trout to the alkaline effluent described on p. 35, para. 5.

The various developmental stages of burbot eggs showed different sensitivities to alkaline waters, the most sensitive stage being that of embryo segmentation, when a pH value of 8.0 killed half the eggs (Volodin, 1960). Resistance increased after this stage, but even at pH 9.0 hatching was delayed. Sperm of common carp had a lower period of motility when the pH value of the water was raised to 8.2–9.5 (Dyk and Lucky, 1956), and pH values above 9.0 were found to be lethal (Elster and Mann, 1950).

2.4.2 FIELD OBSERVATIONS

Fish kills In lakes and rivers, where there exists a combination of high plant density (including algae), high temperature, and strong sunlight, vigorous photosynthetic activity can raise the pH value of the water to high levels for short periods. This is usually followed by lower pH values during the night with minimum values just before dawn. Such a diurnal variation was measured in the R. Tweed in 1956 (Jordan and Lloyd, 1964). These authors point out that the harmful effect of these conditions is determined in part by the length of time for which these high pH values are maintained, and in part by the maximum pH value reached. Other factors include temperature and the high level of dissolved oxygen accompanying the high pH value (p. 35, para. 3). Furthermore, other

possible lethal factors under these conditions are an increase in the dissolved gas content of the water to values greater than atmospheric pressure, which may give rise to 'gas bubble' disease (Doudoroff, 1957), and also certain algal blooms present may produce toxic by-products.

Since the pH values can show a considerable diurnal fluctuation under these natural conditions, it would be necessary to make frequent analyses of the water in order to correlate pH value with fish kills. Eicher (1946) reports that some rainbow trout in a lake were killed when the pH value rose above 10.2, but that fish in a river tolerated a rise to 9.4. For the reasons given above, this observation cannot be correlated directly with laboratory data but it is not at variance with them. Dahl, J. (1957) records a fish kill in L. Lyngby (Denmark) where the pH value rose to 10.3–10.6. In deep lakes, the high pH values may be limited to surface waters only, and fish may be able to survive in the deeper portions where pH values are lower. Mortalities among pike-perch (*Stizostedion lucioperca*) occurred at Ronninge (south of Stockholm) in 1966 when the pH value of the water rose to 8.4–9.5 (T. Hasselrot, personal communication); it is thought, however, that toxins from the accompanying algal bloom may have contributed to the death of the fish.

Natural populations Although Neess (1949), referring to carp ponds at Wielenbach, southern Bavaria, states that a high fish production is maintained there even though the pH value of the water reaches 12, this is an unusually high alkalinity if produced by photosynthetic activity and might be regarded as inaccurate. However, pH values of about 10.0 often occur there during the summer (H. Reichenbach-Klinke, personal communication).

An alkaline discharge to the Austrian Millstätter See raised the pH value of the water to 9.3 over an 8-year period (Findenegg, 1962) but primary productivity appeared to be unaffected although some qualitative changes in the composition of the plankton and fish population were observed.

2.4.3 MODE OF TOXIC ACTION

According to several authors (Kuhn and Koeche, 1956; Bandt, 1936; Schäperclaus, 1956) a toxic action of hydroxyl-ions is to destroy the gill and skin epithelium. Daye and Garside (1976) found that the gills of brook trout were the most sensitive of the surficial tissues to high pH values within a 7-day exposure period, with a threshold pH value of injury of 9.0; mucus cells at the base of the gill filaments became hypertrophic and separation of the epithelium from the pilaster cells occurred at high pH values. Eicher (1946) reported that trout found dying at a pH value of 10.2 (p. 37, para. 2) had frayed dorsal and caudal fins and were blind, and a similar condition was reported by Ivasik (1965) for carp in a heavily weeded pond where the pH value rose to above 9.0, but it is not clear whether these symptoms were a direct result of the high pH value. Damage to the eye lens and cornea of brook trout occurred above a pH value of 9.5 (Daye and Garside, 1976); the lethal pH limit for this species within a 7-day exposure period was 9.8.

2.4.4 AVOIDANCE REACTIONS

Jones (1948) showed that stickleback avoided solutions of sodium hydroxide with a pH value above 11.0 but the range 7–11 produced no avoidance response from fish given the choice between tap water at a pH value of 6.8 and the experimental solutions. Ishio's (1965) results suggest that common carp and goldfish avoid lower levels, the median avoidance pH for these species being 9.30 and 8.64 respectively. However, the comments made by Doudoroff to Ishio's paper mentioned on p. 31, para. 7 are pertinent here also.

2.4.5 EFFECT ON GROWTH

There are no data known to us on the effect of high pH values on the growth rate of fish.

2.4.6 EFFECT ON FOOD SUPPLY

There are no data on the effect of high pH values on food supply of fish apart from the observations by Findenegg (1962) on the Millstätter See (p. 37, para. 4).

2.4.7 TOXICITY OF OTHER POISONS

The section on the effect of low pH values on the toxicity of other poisons is applicable here, in respect of those poisons, such as cyanide and ammonia, whose toxicity is affected by the degree of ionization. This is particularly important in the case of ammonia, the toxicity of which increases with an increase in pH value. Although zinc in solution may be precipitated as the basic carbonate at alkaline pH values, the precipitate can be highly toxic to fish if it is kept in suspension (Lloyd, 1960; Herbert and Wakeford, 1964; Mount, 1966). It is not known whether other heavy metals are toxic when precipitated as basic carbonates.

In summary, it appears that chronic exposure to pH values above 10.0 is harmful to all species studied, while salmonid and some other species are harmed at values above 9.0, and that tentative water quality criteria can be based on the existing data. However, it is difficult to correlate laboratory data with field observations on the effect of alkalinity caused by photosynthetic activity because of the possible additional effect of concomitant high dissolved oxygen levels, and the possibility that the water was also supersaturated with dissolved gases or contained toxic algal by-products, or subsequently became deoxygenated during the hours of darkness. If this problem is sufficiently serious to warrant further research, more attention will have to be given to measuring these factors in the field and making the appropriate laboratory experiments.

Table 2.1 SUMMARY OF THE EFFECTS OF pH VALUES ON FISH

Range	*Effect*
3.0–3.5	Unlikely that any fish can survive for more than a few hours in this range although some plants and invertebrates can be found at pH values lower than this.
3.5–4.0	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, non-lethal levels, but the lower end of this range may still be lethal for roach.
4.0–4.5	Likely to be harmful to salmonids, tench, bream, roach, goldfish and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach and pike, only the last named may be able to breed.
4.5–5.0	Likely to be harmful to the eggs and fry of salmonids, and to adults particularly in soft water containing low concentrations of calcium, sodium and chloride. Can be harmful to common carp.
5.0–6.0	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 mg/ℓ, or the water contains iron salts which are freshly precipitated as ferric hydroxide, the precise toxicity of which is not known. The lower end of this range may be harmful to non-acclimated salmonids if the calcium, sodium and chloride concentrations, or the temperature of the water are low, and may be detrimental to roach reproduction.
6.0–6.5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 mg/ℓ.
6.5–9.0	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9.0–9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9.5–10.0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to developmental stages of some species.
10.0–10.5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10.5–11.0	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11.0–11.5	Rapidly lethal to all species of fish.

Reference is made to different species on the basis of information known to us; the absence of a reference indicates only that insufficient data exist.

2.5 Conclusions

2.5.1 TENTATIVE WATER QUALITY CRITERIA

It is becoming increasingly clear that, for many pollutants, no single level or concentration can be put forward as the dividing line between safe and harmful which is universally applicable for all aquatic situations. Effects of the environment on both the toxicity of the pollutant and the susceptibility of the fish, as well as differences between the susceptibility of the various species of fish and the presence of other pollutants, have to be taken into account when attempting to formulate criteria for safe levels.

Although the existing data on the effect of extreme pH values on fish are neither as comprehensive, nor as accurate, as would be ideally required for the formulation of definite criteria, the information presented in this review does, nevertheless, allow general predictions to be made of the effects of acid or alkaline discharges on a fishery. Such effects are summarized in *Table 2.1*; it should be emphasised that these may have to be revised in the light of future experience and research. Data on avoidance reactions have not been taken into account because of the difficulty in correlating laboratory data with field conditions; also, there is no information on a direct effect of pH value on growth. For the alkaline range, the effect of high levels of dissolved oxygen on the susceptibility of fish has not been considered since there are no relevant quantitative data. There is some evidence that the resistance of fish to extreme pH values increases with age.

2.5.2 SCOPE FOR FURTHER RESEARCH

In order to define water quality criteria more fully, further laboratory research is required on the toxicity to fish of acid waters containing iron salts, and on the growth rates of fish in acid waters. Field studies on the productivity of acid polluted streams are also required. There may be a need for laboratory studies on the effect of high dissolved oxygen levels on the resistance of fish to alkaline pH values, together with those other associated factors which may occur in the field.

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